

Form. Number	Formulation**	Environmental Releases	
		Air (g/sec)	Water or Land (kg/yr)
37	Water	N/A	N/A
	Hydrocarbons, petroleum distillates	0.034	0
	Hydrocarbons, aromatic	0.003	0
38	Hydrocarbons, petroleum distillates	0.048	0
	Alkoxylated alcohols	0.012	0
	Fatty acid derivatives	0	0
39	Water	N/A	N/A
	Hydrocarbons, petroleum distillates	0.015	0
	Propylene glycol ethers	0.008	0
	Alkanolamine	0	17
	Ethylene glycol ethers	0.004	0
40	Hydrocarbons, aromatic	0.009	0
	Hydrocarbons, petroleum distillates	0.012	0
	Fatty acid derivatives	0	346
	Ethoxylated nonylphenol	0	22

**Formulation compositions were adjusted to equal 100 percent.

N/A - Not applicable

3.2 OCCUPATIONAL EXPOSURE ESTIMATES

Inhalation and dermal exposure associated with lithography blanket wash chemicals and the methodology, assumptions and uncertainties associated with the estimates are discussed below. The scenario described below was modelled to assess inhalation and dermal exposures for workers at these shops. Table 3-2 presents the inhalation and dermal exposures for lithographic blanket washes.

Table 3-2. Inhalation and Dermal Exposures: Lithographic Blanket Washes

Form. Number	Formulation ¹	Inhalation Exposure ² (mg/day)	Dermal Exposure ³ (mg/day)
1	Fatty acid derivatives	0.23	1,100-3,300
	Alkoxylated alcohols	0.026	200-590
3	Hydrocarbons, petroleum distillates	7.2	730-2,200
	Fatty acid derivatives	negligible	390-1,200
	Hydrocarbons, aromatic	14.8	121-360
	Alkyl benzene sulfonates	negligible	61-180
4	Terpenes	74	1,100-3,400
	Ethoxylated nonylphenol	negligible	159-480

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Form. Number	Formulation ¹	Inhalation Exposure ² (mg/day)	Dermal Exposure ³ (mg/day)
5	Water Hydrocarbons, petroleum distillates Ethylene glycol ethers Ethoxylated nonylphenol Alkyl benzene sulfonates Alkoxyated alcohols Alkali/ salts	N/A 0.54 0.010 negligible negligible negligible negligible	N/A 340-1,000 170-510 100-300 54-162 27-81 7-20
6	Fatty acid derivatives Hydrocarbons, petroleum distillates Hydrocarbons, aromatic Alkyl benzene sulfonates	negligible 5.4 0.82 negligible	910-2,700 290-880 58-180 37-110
7	Terpenes Ethoxylated nonylphenol Alkoxyated alcohols	2.42 negligible negligible	1,225-3,750 37-110 37-110
8	Water Hydrocarbons, aromatic Propylene glycol ethers Alkyl benzene sulfonate Ethoxylated nonylphenol Alkoxyated alcohols Alkali/ salts	N/A 0.52 0.67 negligible negligible negligible negligible	N/A 290-870 180-530 196-580 87-260 23-70 6-17
9	Fatty acid derivatives Water Ethoxylated nonylphenol	negligible N/A negligible	990-3,000 N/A 25-76
10	Fatty acid derivatives Water	negligible N/A	270-820 N/A
11	Fatty acid derivatives Hydrocarbons, petroleum distillates Hydrocarbons, aromatic Alkyl benzene sulfonates	negligible 7.5 0.63 negligible	670-2,000 540-1,600 54-160 34-100
12	Hydrocarbons, petroleum distillates Water	1.68 N/A	650-1,960 N/A
14	Fatty acids derivatives Propylene glycol ethers Water	negligible 0.009 N/A	98-290 98-290 N/A
16	Terpenes	2.55	1300-4000
17	Ethoxylated nonylphenol Propylene glycol Fatty acid derivatives Alkali/ salts Water	negligible 0.008 negligible negligible N/A	23-68 23-68 11-34 6-17 N/A

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Form. Number	Formulation¹	Inhalation Exposure² (mg/day)	Dermal Exposure³ (mg/day)
18	Fatty acid derivatives Hydrocarbons, petroleum distillates Hydrocarbons, aromatic Dibasic esters Esters/lactones Alkyl benzene sulfonates	negligible 5.8 0.62 0.194 0.68 negligible	640-1,900 430-1,300 57-170 108-330 36-110 36-110
19	Fatty acid derivatives Propylene glycol ethers Water	negligible 0.021 N/A	100-290 260-780 N/A
20	Water Hydrocarbons, petroleum distillates Hydrocarbons, aromatic Alkyl benzene sulfonates	N/A 0.36 0.12 negligible	N/A 130-400 100-300 33-100
21	Hydrocarbons, aromatic Hydrocarbons, petroleum distillates Fatty acid derivatives	2.2 7.1 negligible	260-780 390-1,200 650-2,000
22	Fatty acid derivatives Hydrocarbons, aromatic Water	negligible 0.73 N/A	720-2,100 260-780 N/A
23	Terpenes Nitrogen heterocyclics Alkoxyated alcohols Water	0.83 0.037 0.001 N/A	92-280 57-170 57-170 N/A
24	Terpenes Ethylene glycol ethers Ethoxylated nonylphenol Alkyl benzene sulfonates Alkali/salts Water	2.3 0.002 negligible negligible negligible N/A	210-620 52-160 52-160 78-230 52-160 N/A
25	Terpenes Esters/lactones	2.11 2.4	1,248-3,840 52-160
26	Fatty acid derivatives Esters/lactones	negligible negligible	1,219-3,758 45-135
27	Terpenes	4.69	1,300-3,900
28	Hydrocarbons, petroleum distillates	240	1,300-3,900
29	Fatty acid derivatives	negligible	1,300-3,900
30	Hydrocarbons, aromatic Propylene glycol ethers Water	1.9 0.026 N/A	910-2,700 130-390 N/A
31	Hydrocarbons, aromatic Hydrocarbons, petroleum distillates	0.88 11	200-590 1,100-3,300
32	Hydrocarbons, petroleum distillates	24	1,300-3,900

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Form. Number	Formulation ¹	Inhalation Exposure ² (mg/day)	Dermal Exposure ³ (mg/day)
33	Hydrocarbons, petroleum distillates	0.93	310-920
	Hydrocarbons, aromatic	0.44	310-920
	Propylene glycol ethers	0.068	34-100
	Water	N/A	N/A
34	Water	N/A	N/A
	Terpenes	3.3	230-680
	Hydrocarbons, petroleum distillates	0.56	170-510
	Alkoxylated alcohols	negligible	85-250
	Fatty acid derivatives	negligible	85-250
35	Hydrocarbons, petroleum distillates	11	200-590
	Hydrocarbons, aromatic	0.88	1,100-3,300
36	Fatty acid derivatives	negligible	900-2,700
	Hydrocarbons, petroleum distillates	4.1	230-680
	Hydrocarbons, aromatic	1.0	110-340
	Propylene glycol ethers	0.37	57-170
37	Water	N/A	N/A
	Hydrocarbons, petroleum distillates	1.67	625-1,840
	Hydrocarbons, aromatic	0.064	32-97
38	Hydrocarbons, petroleum distillates	10	980-2,900
	Alkoxylated alcohols	0.022	200-590
	Fatty acid derivatives	negligible	130-390
39	Water	N/A	N/A
	Hydrocarbons, petroleum distillates	0.60	220-670
	Propylene glycol ethers	0.31	110-330
	Alkanolamines	negligible	30-89
	Ethylene glycol ethers	0.003	52-160
40	Hydrocarbons, aromatic	1.4	130-380
	Hydrocarbons, petroleum distillates	4.0	190-570
	Fatty acid derivatives	negligible	950-2,800
	Ethoxylated nonylphenol	negligible	38-110

¹ Formulation compositions were adjusted to equal 100 percent.

² The inhalation exposures are based on a "what if" scenario.

³ The dermal exposures are bounding estimates and assume that no gloves or barrier creams are used by the workers.

⁴ In situations where the chemical is corrosive (e.g., sodium hydroxide), dermal exposure to workers using the appropriate gloves is zero.

Negligible - Inhalation exposures to chemicals with vapor pressures <10⁻³ mmHg were assumed negligible.

N/A - Not applicable

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Scenario

Based on the general facility assumptions listed in Section 3.1, a press operator is assumed to wash 40 blankets per shift. Each wash lasts two minutes. The worker squirts 2 ounces of wash solution onto a rag using a squirt bottle. The blanket is wiped with the wet rag and then wiped again with a dry rag. All rags are disposed of in closed storage containers.

Inhalation exposures result from the volatilization of chemicals from the blanket during washing and from the rags used to wash the blanket. Unvolatilized materials that remain on the rags are assumed to be disposed of as solid waste or to be removed at a laundry facility. Inhalation exposures to vapors from opening the containers storing the disposed rags are assumed to be negligible. Inhalation exposures to chemicals with a vapor pressure $< 10^{-3}$ mm Hg are also assumed to be negligible.

Dermal exposures result from contact with the blanket wash solution during blanket washing activities. Dermal exposures are estimated based on type of operations and wash formulation concentrations.

Methodology - Inhalation Exposures

Inhalation exposures were estimated from the scenario described above using a material balance inhalation exposure model^b. The inhalation exposure assessment falls under the "what if" category (see uncertainties section).

The material balance model assumes that the amount of a chemical in a room equals the amount of chemical generated in the room minus the amount of chemical leaving the room. The model is valid for estimating the displacement of vapors from containers and for estimating the volatilization of liquids from open surfaces. The assumptions used in this model include:

- Incoming room air is contaminant-free;
- Vapor generation and ventilation rates are constant over time;
- Room air and ventilation air mix ideally;
- Raoult's Law is valid (i.e., regarding the volatilization and interaction of vapors);
- Ideal gas law applies (i.e., regarding the interaction of vapors); and
- "Typical case" ventilation parameters are valid (actual ventilation conditions are unknown).

The inhalation exposure model¹ estimates the evaporation of chemicals from open surfaces, such as the surface of a blanket, using the following equations:

^b Source: U.S. Environmental Protection Agency, Chemical Engineering Branch (CEB) Manual for the Preparation of Engineering Assessments, (February 28, 1991), p. 4-1 through 4-39.

$$G_i = \frac{0.02MX_iP_i}{RT} \sqrt{\frac{D_{ab}v_z}{\pi z}} \quad (1)$$

where:

G_i	=	Volatilization rate of subsurface i, g/m ² ·sec
M	=	Molecular weight, g/mol
P_i^*	=	Vapor pressure of pure substance i, mm Hg
X_i	=	Mole fraction of substance i in solution, dimensionless
R	=	Gas constant, 0.0624 mm Hg·m ³ /mol·K
T	=	Temperature, K
D_{ab}	=	Diffusivity, cm ² /sec
v_z	=	Air velocity, m/sec
z	=	Distance along contaminated surface, m

The air velocity v_z is assumed to be 100 feet per minute (ft/min). Since the diffusivity (D_{ab}) is not available for many of the chemicals used in blanket washing formulations, the following equation is used to estimate diffusivity:

$$D_{ab} = \frac{4.09 \times 10^{-5} T^{1.9} (1/29 + 1/M)^{0.5} M^{0.33}}{P_t} \quad (2)$$

D_{ab}	=	Diffusivity, cm ² /sec
T	=	Temperature, K
M	=	Molecular weight, g/mol
P_t	=	Total pressure, atm

Equation 2 is based on kinetic theory and generally gives values of D_{ab} that agree closely with experimental data. The volatilization rate (G_i), calculated in Equations 1 and 2 above, is used in the following mass balance equation to calculate the airborne concentration of a substance in the breathing zone:

$$C_v = \frac{1.7 \times 10^5 TG_i A}{MQk} \quad (3)$$

where:

C_v	=	Airborne concentration, ppm
T	=	Ambient temperature, K
G_i	=	Volatilization rate of substance i, g/m ² ·sec
M	=	Molecular weight, g/mol
A	=	Area of surface, m ²
Q	=	Ventilation rate, ft ³ /min
k	=	Mixing factor, dimensionless

The mixing factor (k) accounts for slow and incomplete mixing of ventilation air with room air. The CEB Manual sets this factor at 0.5 for a typical case and at 0.1 for a worst case.

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The CEB Manual commonly uses ventilation rates (Q) of 500 to 3,500 ft³/min. An effective ventilation rate of 1,500 ft³/min was used in the model. This rate is equal to the mixing factor of 0.5 multiplied by the "typical case" ventilation rate (3,000 ft³/min). The value of C_v from Equation 3 is converted to mass/volume units using the following equation:

$$C_m = C_v \frac{M}{V_m} \quad (4)$$

where:

C _m	=	Airborne concentration, mg/m ³
C _v	=	Airborne concentration, ppm
M	=	Molecular weight, g/mol
V _m	=	Molar volume of an ideal gas, L/mol

At 25°C, V_m has a value of 24.45 L/mol. Since a worker can be assumed to breathe about 1.25 m³ of air per hour, an inhalation exposure can be computed once C_m has been determined. Equations 3 and 4 can be combined to yield the following equation, given the "typical case" choice of ventilation parameters:

$$I = 0.48GAt \quad (5)$$

where:

I	=	Total amount of substance inhaled, mg/day
G	=	Vapor generation rate, g/m ² ·sec
A	=	Area of surface, m ²
t	=	Duration of exposure, sec/day

The following variables for the lithography model shop are based on the Chemical Engineering Branch Manual (EPA, 1991)¹¹

- v_z = 100 ft/min (air velocity)
- T = 298 K (temperature)
- Q = 3,000 ft³/min (ventilation rate)
- k = 0.5 (mixing factor, dimensionless)
- P_i = X_i·P_i^{*} (Raoult's Law)

The following variables are based on the assumptions presented on page 3-2. These assumptions were reviewed during the ECB/GATF Environmental Affairs Conference held in Oakbrook, Illinois in March, 1994.

- z = 26 in (distance along contaminated surface)
- A = 494 in² (area of surface)
- The average time to wash one blanket is 2 minutes.

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- The average number of blankets washed per shift is 40.
- The average worker is exposed to wash vapors 80 minutes per day (t = 4,800 seconds per day).
- Dilutions with water are accounted for in formulation compositions.
- Adjusted values were used for the formula compositions because they did not always sum to 100%.

Sample Calculation - Inhalation Exposures

Example Formulation (compositions are percent by weight):

Range	Adjusted*	
35-45%	42.9%	Ethoxylated nonylphenol
25-35%	33.3%	Solvent naphtha (petroleum), heavy aromatic
15-20%	19.0%	Propylene glycol monobutyl ether
0-5%	4.8%	Tetrapotassium pyrophosphate
75-105%	100%	Total

* In cases where the maximum range values of the chemical compositions did not add up to 100%, the values were adjusted to 100%.

The diffusivity is calculated using Equation 2, as follows:

$$D_{ab} = \frac{4.09 \times 10^{-5} T^{1.9} (1/29 + 1/M)^{0.5} M^{-0.33}}{P_t}$$

The following values are obtained from the Basic Chemical Data Report for solvent naphtha (petroleum), heavy aromatic:

T = 298 K
M = 128 g/mol
P_t = 1 atm

$$D_{ab} = 0.085 \text{ cm}^2/\text{sec}$$

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Using the above value for diffusivity, the volatilization rate can be calculated using Equation 1, as follows:

$$G_i = \frac{0.02MX_iP_i}{RT} \sqrt{\frac{D_{ab}v_z}{\pi z}}$$

where:

M	=	128 g/mol
P _i	=	0.5 mm Hg
X _i	=	0.5346 (mole fraction)
R	=	0.0624 mm Hg·m ³ /mol·K
T	=	298 K
D _{ab}	=	0.0852 cm ² /sec
v _z	=	100 ft/min = 0.508 m/sec
z	=	26 in = 0.6604 m

$$G_i = 0.0053 \text{ g/m}^2\cdot\text{sec}$$

Using this value for G_i, the exposure may be calculated using Equation 5, as follows:

$$I = 0.48GA t$$

where:

G	=	0.0053 g/m ² ·sec
A	=	494 in ² = 0.3187 m ²
t	=	80 min = 4,800 sec/day

$$I = 3.9 \text{ mg/day}$$

Using the same method for each chemical in the Example Formulation, the following results are obtained:

Chemical	Inhalation Rate
Ethoxylated nonylphenol	Negligible
Solvent naphtha (petroleum), heavy aromatic	3.9 mg/day
Propylene glycol monobutyl ether	4.3 mg/day
Tetrapotassium pyrophosphate	Negligible

Methodology - Dermal Exposures

Dermal exposure is caused by contact with a material. For the blanket press operators, contact with the material includes touching the damp rags and manually applying the rags to the blanket to remove ink. Routine contact with two hands was modeled for the dermal exposure assessment.

The dermal contact model¹ was used to calculate dermal exposure estimates for blanket washing activities by adjusting the concentration of the chemical in the mixture. This model provides bounding estimates and assumes that no gloves or barrier creams are used by the workers. In situations where the chemical is corrosive (e.g., sodium hydroxide), dermal exposure to workers using the appropriate gloves is negligible. Also, for other chemicals, if the appropriate gloves are worn exposure to workers will be negligible.

Assumptions used in the dermal model¹ include:

- The concentrations of the chemicals in the mixture are constant (i.e., no evaporation) throughout the time of absorption;
- No dermal protection, administrative, work practice, or other controls are used to limit dermal exposure;
- The surface area of two hands is 1300 cm²;
- The amount that is actually absorbed is not determined;
- The quantity remaining on the hand is 1-3 mg/cm²; and
- A single contact with the chemical results in exposure for a complete work day. That is, the duration of exposure is estimated at 1-4 hours or longer, but it is assumed the worker washes up at meal time, and if the duration is reported for a full day, the potential dose should total only the estimate for a single contact.

Sample Calculation - Dermal Exposures

Using the Example Formulation:

Ethoxylated nonylphenol = 42.9% (Adjusted weight %)

The dermal exposure to blanket washes for routine dermal contact (2 hands) is 1,300 to 3,900 mg/day¹. (e.g., 1-3 mg/cm² x 1300 cm²/day)

The dermal exposure to ethoxylated nonylphenol is 42.9% of the total blanket wash exposure, or 560 to 1,700 mg/day.

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Using the same method for each chemical in the Example Formulation, the following results are obtained:

Chemical	Dermal Exposure
Ethoxylated nonylphenol	560 to 1,700 mg/day
Solvent naphtha (petroleum), heavy aromatic	430 to 1,300 mg/day
Propylene glycol monobutyl ether	250 to 740 mg/day
Tetrapotassium pyrophosphate	62 to 190 mg/day

Uncertainties - Occupational Exposures

Any determination of the occupational exposure levels associated with blanket washing activities requires making assumptions about the washing processes, workplace environment, health and safety practices, and waste management practices.

EPA has published Guidelines for Exposure Assessment in the *Federal Register*. These guidelines provide the basic terminology and principles by which the Agency conducts exposure assessments. If the exposure assessment methodology allows an assessor to in some way quantify the spectrum of exposure, the assessor should assess typical exposures, as well as high-end exposures or bounding exposures. **Typical** exposures refer to exposures of a typical person to a particular substance. **High-end** exposures refer to exposures of a person exposed to amounts of a substance higher than exposures received by 90 percent of the people (or ecological species of interest) exposed to the substance. **Bounding** exposures are judgments assuming that no one will be exposed to amounts of substance higher than the calculated amount. However, in many cases, only a picture of what the exposure would be under a given set of circumstances, without a characterization of the probability of these circumstances, can be calculated. These pictures are called "**What if**" scenarios,^c and they do not try to judge where on the exposure scale the estimate actually falls. The inhalation exposure assessments calculated for the blanket press operators fall under the "what if" category and the dermal exposure assessments are bounding exposures.

Although the blanket washing process is relatively straightforward, occupational exposure levels will differ in shop environments because of many variables, including:

- Volatility of blanket wash used;
- Amount of blanket wash applied;
- Application of chemicals to blanket and rags;
- Use of personal protective equipment and safety procedures;
- Blanket washing time;
- Ventilation conditions and shop layout;
- Number of blankets cleaned;
- Temperature conditions (ambient and solvent);
- Average size of blankets; and
- Number of presses per facility.

^c A "what-if scenario" is a scenario developed to assess potential exposure under a set of hypothetical conditions or under a set of conditions for which actual exposure parameter data are incomplete or nonexistent. The calculated exposures are not intended to provide information about how likely the combination of exposure parameter values might be in the actual population or approximately how many, if any, persons might actually be subjected to the calculated exposure.